Spatial decay of the single-particle density matrix in tight-binding metals: analytic results in two dimensions

S. N. Taraskin,[1,*] P. A. Fry,[2,†] Xiaodong Zhang,[3,‡] D. A. Drabold,[3,§] and S. R. Elliott[1,¶]

[1]*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*
[2]*St.John's College, University of Cambridge, St. John's St., Cambridge CB2 1TP, UK*
[3]*Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701*

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Analytical results for the asymptotic spatial decay of the density matrix $\rho(\mathbf{r},\mathbf{r}')$ in the tight-binding model of the two-dimensional metal are presented. In various dimensions D, it is found analytically and numerically that the density matrix decays with distance according to the power law, $\rho(\mathbf{r},\mathbf{r}') \propto |\mathbf{r}-\mathbf{r}'|^{-(D+1)/2}$.

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The computation of ground-state properties of a condensed-matter system from the electronic structure depends critically upon the computation of the single-particle density matrix (DM). If one possesses the occupied eigenstates $\psi_i(\mathbf{r})$ of a single-particle Hamiltonian $\hat{\mathbf{H}}$, then the density matrix at zero temperature can be expressed as $\rho(\mathbf{r},\mathbf{r}') = \sum_{i\ \mathrm{occupied}} \psi_i^*(\mathbf{r}')\psi_i(\mathbf{r})$. The diagonal element of the DM, $\rho(\mathbf{r},\mathbf{r})$, is the charge density. The electronic energy may be expressed as $\mathrm{Tr}(\hat{\boldsymbol{\rho}}\hat{\mathbf{H}})$, and in a simple case the electronic part of the interatomic forces may be expressed as $\mathrm{Tr}(-\hat{\boldsymbol{\rho}}\partial\hat{\mathbf{H}}/\partial\mathbf{R})$, where $\mathbf{R}$ is an atomic coordinate. Viewed in the position representation, it is clear that the decay of $\rho(\mathbf{r},\mathbf{r}')$ determines how *locally* one can formulate a calculation of the energy or forces. This is of special interest in so-called "quantum order-N" methods in modern first-principles computational condensed-matter physics [1, 2].

The DM provides a means to differentiate between a metallic and an insulating state. A considerable body of work has been devoted to computing the DM in various systems. For insulators, it is well established that, for $|\mathbf{r}-\mathbf{r}'| \to \infty$, $\rho(\mathbf{r},\mathbf{r}') \sim \exp(-\gamma|\mathbf{r}-\mathbf{r}'|)$ [3, 4]. Recently, we have published detailed asymptotic expansions for insulators in one, two and three dimensions [5]. In *metals* the situation is less clear. Analytic results are available for the free-electron gas in any dimensionality ($D = 1-3$) and the DM exhibits a power-law decay with Gibbs ringing (from the abrupt cutoff at the Fermi surface at $T = 0$) [6]. Little is known about the "tight-binding" case, except in one dimension where the mathematics is trivial. One more "realistic" numerical calculation with a density functional Hamiltonian has appeared for Al, which produces a DM quite similar to the free-electron gas[7]. In this Brief Report, we provide analytical asymptotic results for the decay of the DM in one dimension and, for the first time, in two dimensions for special directions on a square lattice. The DM is found to decay generally as $|\mathbf{r}-\mathbf{r}'|^{-(D+1)/2}$ for large $|\mathbf{r}-\mathbf{r}'|$, which coincides with the free-electron case. Numerics support this law for all three dimensions along various lattice directions. We provide detailed expressions for the decay depending upon the parameters of the one-band tight-binding model and the position of the Fermi level. The analytic results are confirmed by direct numerical evaluation of the DM.

Let us consider a tight-binding Hamiltonian defined on a lattice,

$$\hat{\mathbf{H}} = \sum_i^N \varepsilon_i |i\rangle\langle i| + \sum_{i\neq j}^N t_{ij}|i\rangle\langle j| \ , \qquad (1)$$

where the orthonormal site basis $|i\rangle$ (one electron orbital per site) spans the Hilbert space of the state vectors. In the case analyzed below, all the site energies, $\varepsilon_i = \varepsilon$, and transfer integrals between nearest neighbours, $t_{ij} = t$, are constant through the lattice. The Bloch functions, $|\mathbf{k}\rangle = N^{-1/2}\sum_j \exp\{i\mathbf{k}\cdot\mathbf{R_j}\}|j\rangle$, with dispersion $\varepsilon_{\mathbf{k}} = 2t\sum_\alpha^D \cos(k_\alpha a)$ for the simple cubic lattice (say, with lattice constant $a = 1$ and $\varepsilon = 0$) solve the eigenproblem for the Hamiltonian (1).

The object to evaluate is the density-matrix operator, $\hat{\boldsymbol{\rho}}$, which can be written in the momentum representation as $\hat{\boldsymbol{\rho}} = \sum_{\mathbf{k}} |\mathbf{k}\rangle f_{\mathbf{k}} \langle\mathbf{k}|$, with $f_{\mathbf{k}}$ being the occupation probabilities for different eigenstates. For an electronic system in thermal equilibrium, these probabilities are the Fermi-Dirac factors, $f_{\mathbf{k}} = f(\varepsilon_{\mathbf{k}}) = (1+\exp\left[(\varepsilon_{\mathbf{k}}-\mu)/T\right])^{-1}$, where μ is the Fermi level and T is the temperature. The matrix elements of the density-matrix operator in the site basis, $\rho_{ij} = \langle i|\hat{\boldsymbol{\rho}}|j\rangle$, are of special interest for obtaining the decay properties of the DM in real space. These matrix elements can be written in terms of the matrix elements of the Green's function operator, $G_{ij}(\varepsilon) = \langle i|(\varepsilon - \hat{\mathbf{H}})^{-1}|j\rangle$, as:

$$\begin{aligned}\rho_{ij} &= \frac{1}{N}\int_{-\infty}^{\infty} f(\varepsilon)\sum_{\mathbf{k}}\delta(\varepsilon-\varepsilon_{\mathbf{k}})\exp\{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_i)\}\mathrm{d}\varepsilon \\ &= -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\infty} f(\varepsilon)G_{ij}(\varepsilon+i0)\mathrm{d}\varepsilon \ . \qquad (2)\end{aligned}$$

The problem of the DM decay is thus partly reduced to the problem of the evaluation of the off-diagonal elements

of the Green's function operator in the site basis, which is known to be not at all an easy task (see e.g. Ref. [8] and references therein). After some standard algebraic manipulations and introducing auxiliary integration (see e.g. [9]), the expression for $G_{ij} \equiv G_{\nu_\alpha}$ for the simple cubic lattice can be recast in the following form:

$$G_{\nu_\alpha}(\varepsilon) = -\frac{i}{2t}\int_0^\infty \exp\{iz\varepsilon/2t\}\prod_\alpha^D i^{\nu_\alpha} J_{\nu_\alpha}(z)\mathrm{d}z \ , \quad (3)$$

where the integers ν_α stand for the Cartesian projections of the connection vector $\mathbf{R}_j - \mathbf{R}_i$, and $J_\nu(z)$ is the Bessel function.

Starting from this point, we are able to proceed analytically further only in the particular case of a square lattice ($D = 2$) along the main diagonal, $\nu_x = \nu_y \equiv \nu$ (and in the one-dimensional case as well), when the integral over z can be taken exactly [10]:

$$\int_0^\infty \exp\{iz\varepsilon/2t\}J_\nu^2(z)\mathrm{d}z = \frac{1}{\pi}Q_{\nu-1/2}(1-2\epsilon^2) + \frac{i}{2}P_{\nu-1/2}(1-2\epsilon^2) \ , \quad (4)$$

if the energy belongs to the band region, $0 < |\epsilon| < 1$, where $\epsilon \equiv \varepsilon/4t$. The functions P_ν and Q_ν are the associated Legendre functions of the first and second kind, respectively. The expression for the DM can then be recast as

$$\rho_\nu = (-1)^\nu \frac{2}{\pi}\int_{-1}^{\epsilon_\mathrm{F}} Q_{\nu-1/2}(1-2\epsilon^2)\mathrm{d}\epsilon \ , \quad (5)$$

where $\epsilon_\mathrm{F} \equiv \mu/4t$ is the dimensionless Fermi level and the zero-temperature case is implied. If the Fermi level lies above the band, i.e. $\epsilon_\mathrm{F} \geq 1$, all the states are occupied at zero temperature and the DM is $\rho_\nu = \delta_{\nu 0}$, just reflecting the completeness of the basis set. This property, together with the even character of the integrand in Eq. (5), allows us to rewrite the expression for the DM (for $\nu > 0$) in the following form:

$$\rho_\nu = (-1)^\nu \frac{2}{\pi}\int_{0}^{\epsilon_\mathrm{F}} Q_{\nu-1/2}(1-2\epsilon^2)\mathrm{d}\epsilon \ , \quad (6)$$

and consider for definiteness only $\epsilon_\mathrm{F} > 0$.

The integral in Eq. (6) can be simplified in the asymptotic limit of large $\nu \to \infty$ by using the asymptotic expression for $Q_{\nu-1/2}(\cos\phi)$ [10],

$$Q_{\nu-1/2}(\cos\phi) \simeq \sqrt{\frac{\pi}{2\nu\sin\phi}}\cos\left(\nu\phi + \frac{\pi}{4}\right) \ , \quad (7)$$

where $\phi = \cos^{-1}(1-2\epsilon^2)$, so that

$$\rho_\nu \simeq \frac{(-1)^\nu}{2\pi^{3/2}\nu^{1/2}}\int_0^{\phi_0}\sqrt{\frac{\sin\phi}{1-\cos\phi}}\cos\left(\nu\phi+\frac{\pi}{4}\right)\mathrm{d}\phi \ , \quad (8)$$

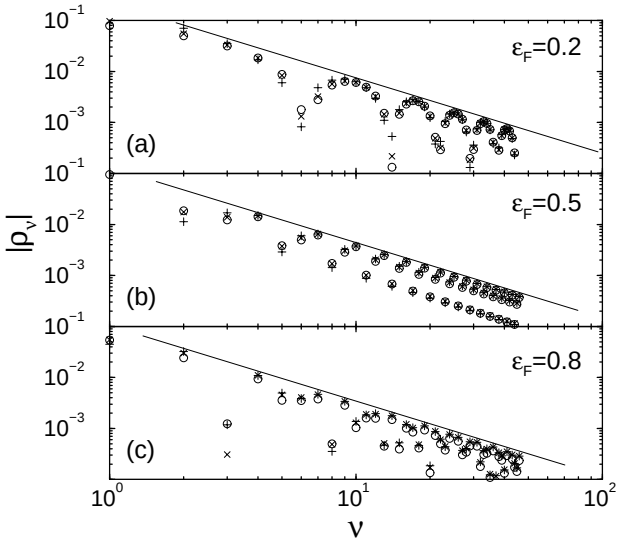

FIG. 1: The dependence of the absolute value of the DM, $|\rho_\nu|$, on the lattice index ν along the main diagonal $[1,1]$ in the square lattice ($\mathbf{R}_j - \mathbf{R}_j = (\nu_x, \nu_y) \equiv (\nu,\nu)$) for a tight-binding model of a crystalline metal at zero temperature and various positions of the Fermi-level, $\epsilon_\mathrm{F} = \mu/4t$, as marked in (a)-(c). The open circles represent the exact numerical result obtained from Eq. (2). The crosses and pluses correspond to the approximate results obtained by using Eqs. (9) and (11), respectively. The straight solid lines show the power-law dependence, $\rho_\nu \propto \nu^{-3/2}$.

with $\phi_0 = \cos^{-1}(1-2\epsilon_\mathrm{F}^2)$. The final step revealing the explicit asymptotic dependence of the DM on ν can be made if the Fermi level lies not far from the midband point and $\phi_0 \ll 1$. In that case, the first term of the integrand in Eq. (8) can be expanded in ϕ, resulting in

$$\rho_\nu \simeq (-1)^\nu \frac{\sqrt{2}}{\pi^{3/2}\nu}\int_0^{\psi_0}\cos\left(\psi^2+\frac{\pi}{4}\right)\mathrm{d}\psi \ , \quad (9)$$

with $\psi_0 = \sqrt{\nu\phi_0}$. All the non-trivial dependence on ν is now in the upper limit of the integral, the latter being proportional to the Fresnel integrals $C(x)$ and $S(x)$,

$$\rho_\nu \simeq (-1)^\nu \frac{1}{\pi\nu\sqrt{2}}\left[C(\sqrt{2\nu\phi_0/\pi}) - S(\sqrt{2\nu\phi_0/\pi})\right] \ , \quad (10)$$

and in the asymptotic limit, $\sqrt{2\nu\phi_0/\pi} \to \infty$ [10],

$$\rho_\nu \simeq (-1)^\nu \frac{1}{(\pi\nu)^{3/2}\sqrt{2\phi_0}}\cos\left(\nu\phi_0 - \frac{\pi}{4}\right) \ . \quad (11)$$

As follows from Eq. (11), the DM decays according to the power law, $\rho_{ij} \propto |\mathbf{R}_j - \mathbf{R}_i|^{-3/2}$, at least along the main diagonal in the square lattice.

All the analytical results presented above can be verified by direct numerical analysis. In Figs. 1(a)-(c), we show the dependence of the DM versus ν along the diagonal $[1,1]$ in the square lattice for different positions of the Fermi level. The exact numerical results (open circles) have been obtained by both direct summation over

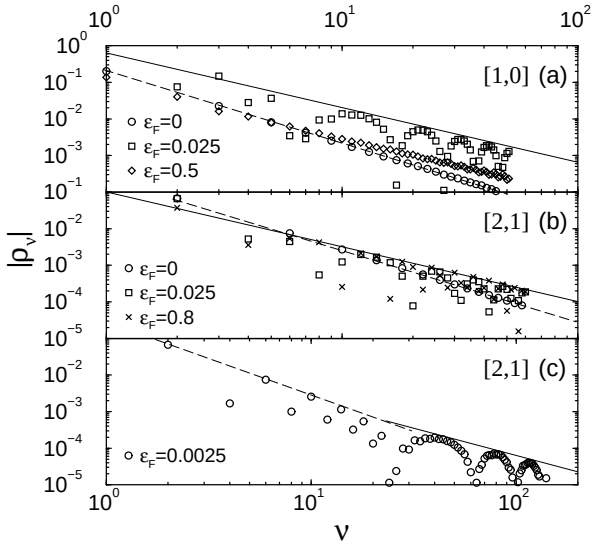

FIG. 2: The dependence of the absolute value of the DM, $|\rho_\nu|$, on the lattice index ν: (a) along the direction $[1,0]$ in the square lattice ($\mathbf{R}_j - \mathbf{R}_j = (\nu_x, 0) \equiv (\nu, 0)$) and (b)-(c) along the direction $[2,1]$ in the square lattice ($\mathbf{R}_j - \mathbf{R}_j = (2\nu_y, \nu_y) \equiv (2\nu, \nu)$) for the same model as in Fig. 1. The results are obtained numerically from Eq. (2). The straight solid and dashed lines show the power-law dependences, $\rho_\nu \propto \nu^{-3/2}$ and $\rho_\nu \propto \nu^{-2}$, respectively.

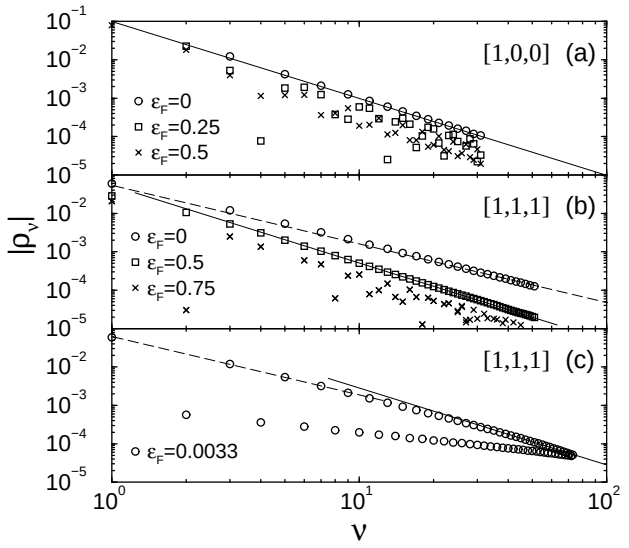

FIG. 3: The dependence of the absolute value of the DM, $|\rho_\nu|$, on the lattice index ν: (a) along the direction $[1,0,0]$ in the simple cubic lattice ($\mathbf{R}_j - \mathbf{R}_j = (\nu_x, 0, 0) \equiv (\nu, 0, 0)$) and (b)-(c) along the direction $[1,1,1]$ in the simple cubic lattice ($\mathbf{R}_j - \mathbf{R}_j = (\nu_x, \nu_y, \nu_z) \equiv (\nu, \nu, \nu)$) for a tight-binding model of a crystalline metal at zero temperature and various positions of the Fermi level, $\epsilon_\mathrm{F} = \mu/8t$, as marked. The results are obtained numerically from Eq. (2). The straight solid and dashed lines show the power-law dependences, $\rho_\nu \propto \nu^{-2}$ and $\rho_\nu \propto \nu^{-3/2}$, respectively.

the first Brillouin zone in Eq. (2) (over 10^8 points) and by integration of Eq. (5) (both methods give identical results). The approximate analytic results according to Eqs. (9) and (11) are given by the crosses and pluses, respectively. Good agreement between the exact and approximate dependencies is evident, even for the relatively large values of the Fermi-level position far away from the midband region (see Fig. 1(c)). The solid straight lines in Fig. 1 corresponding to the power law, $|\rho_\nu| \propto \nu^{-3/2}$, confirm the same law for the DM decay.

In order to verify the power-law decay of the DM along other directions in the simple square lattice, we have calculated the DM numerically for these directions and have found the same asymptotic behavior, $\rho_\nu \propto \nu^{-3/2}$. The results for directions $[1,0]$ and $[2,1]$ and different positions of the Fermi level are presented in Figs. 2(a)-(c).

For the special case that the Fermi level lies exactly at the band center, $\epsilon_\mathrm{F} = 0$, note that for the main diagonal $[1,1]$, the DM vanishes for $\nu > 0$ (see Eq. (6)). This behavior is also manifested in other directions: for $\epsilon_\mathrm{F} \approx 0$ from $\rho_\nu \propto \nu^{-3/2}$ to $\rho_\nu \propto \nu^{-2}$ (see the dashed lines in Figs. 2(a)-(b)). Fig. 2(c) shows how this occurs for the direction $[2,1]$ when $\epsilon_\mathrm{F} \to 0$.

The analysis of the DM decay in different dimensions can be performed analytically for $D = 1$ and numerically for $D = 3$. First, we look at the one-dimensional system. In the case of zero temperature, the integrals in Eq. (2) can be taken exactly, resulting in the following expression for the DM ($|\mu/2t| \leq 1$):

$$\rho_\nu = \frac{1}{\pi\nu} \sin\left[\nu\left(\sin^{-1}\frac{\mu}{2t} + \frac{\pi}{2}\right)\right] . \qquad (12)$$

This expression has the correct limits for a fully occupied ($\mu = 2t$) and an empty ($\mu = -2t$) band, viz. $\rho_\nu = \delta_{\nu 0}$ and $\rho_\nu = 0$, respectively, and shows the power-law decay, $\rho_\nu \propto \nu^{-1}$. Bearing in mind the decay law, $\rho_\nu \propto \nu^{-3/2}$, found for $D = 2$, we can infer that the generalized law in all dimensions is:

$$\rho_{ij} = \rho_\nu \propto \nu^{-(D+1)/2} \propto |\mathbf{R}_j - \mathbf{R}_i|^{-(D+1)/2} . \qquad (13)$$

In order to check Eq. (13) for $D = 3$, we have calculated numerically the DM for the simple cubic lattice along different directions for various positions of the Fermi level. The results are shown in Figs. 3(a)-(c), from which it is clear that indeed the DM asymptotically satisfies Eq. (13) and $\rho_\nu \propto \nu^{-2}$.

Similar to the $2D$-case, the mid-band location of the Fermi energy brings additional symmetry to the problem which can change the asymptotic behaviour of the DM along certain directions. For example, if $\epsilon_\mathrm{F} = 0$ then $\rho_\nu = 0$ for $\nu > 0$ along the direction $[1,1,0]$ and $\rho_\nu \propto \nu^{-3/2}$ along the $[1,1,1]$ direction (see the dashed line in Fig. 3(b); Fig. 3(c) demonstrates how the new asymptotic behavior appears when the Fermi level approaches the midband position).

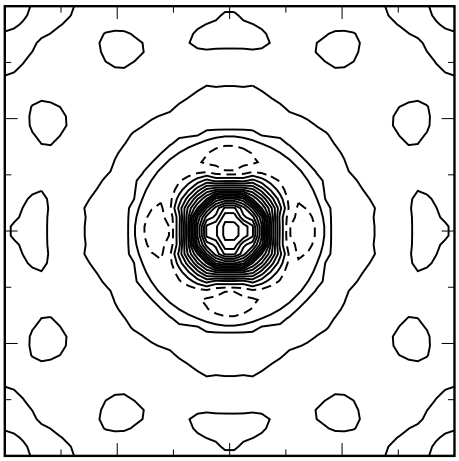

FIG. 4: Contour plot of the real-space density matrix for Al calculated in the {100} plane for the conventional cubic unit cell (the $x-y$ axes are parallel to the bonds).

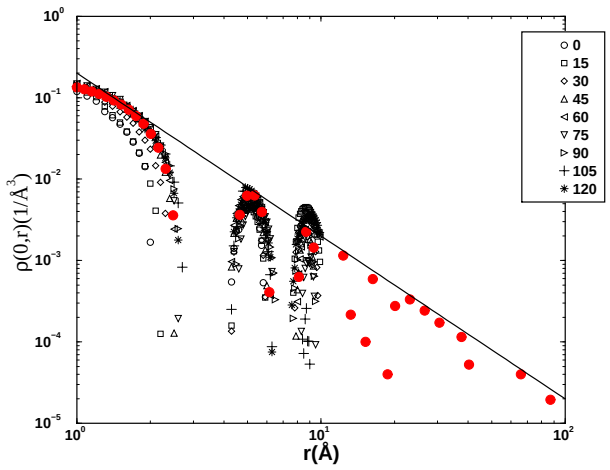

FIG. 5: Spatial decay of the real-space density matrix for Al calculated for different angular directions, as marked (zero angle refers to the bond direction), in the {100} plane for the conventional cubic unit cell. The solid circles represent calculated values of the density matrix for the free-electron gas model with the same electron density as for Al. The solid line shows an r^{-2} dependence.

The above analytical and numerical results have been obtained for very simple tight-binding models. This of course leaves open the question about the generality of our findings. In order to answer this question, at least to some extent, we have calculated the single-electron DM for a realistic model of fcc aluminum (500 atom supercell with the box side of $20.25\mathbf{r}A$) using an approximate density functional Hamiltonian in the local density approximation (see Ref. [7] for more detail). The results are presented in Figs. 4 and 5. The real-space contour plot for the DM in the {100} plane for the conventional cubic unit cell is shown in Fig. 4. From this plot, we can see the isotropic metallic nature of the bonding, in contrast to the case of semiconductors with covalent bonding (cf. Fig. 3 in Ref. [7]). The spatial decay of the DM along different directions in the same symmetry plane for Al is shown in Fig. 5, together with the data calculated for the free-electron gas model [6] (with the electron density being the same as that for Al, i.e. $0.185\mathbf{r}A^{-3}$). It is clearly seen that the DM for Al decays in a very similar fashion to that for the free-electron gas model, i.e. $\rho \propto r^{-2}$. Therefore, these results support the generality of our model calculations.

In conclusion, we have presented analytical and numerical arguments supporting the power-law decay of the density matrix, $\rho_{ij} \propto |\mathbf{R}_j - \mathbf{R}_i|^{-(D+1)/2}$, in tight-binding models of metals in different dimensions at zero temperature. The main result is the analytical asymptotic dependence of the density matrix versus distance along the main diagonal in the square lattice (see Eq. (11)). Apparently, the sharp cutoff induced by the Fermi-Dirac distribution at zero temperature in the integration over the energy spectrum, independently of the shape of the density of states, results in the power-law decay of the density matrix in crystalline metals.

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* Electronic address: snt1000@cus.cam.ac.uk
† Electronic address: paf25@cam.ac.uk
‡ Electronic address: xzhang@helios.phy.ohiou.edu
§ Electronic address: drabold@ohio.edu; Work implemented while on leave at Trinity College, Cambridge
¶ Electronic address: sre1@cus.cam.ac.uk

[1] W. Kohn, Phys. Rev. Lett. **76**, 3168 (1996).
[2] S. Goedecker, Rev. Mod. Phys. **71**, 1085 (1999).
[3] S. Ismail-Beigi and T. A. Arias, Phys. Rev. Lett. **82**, 2127 (1999).
[4] L. He and D. Vanderbilt, Phys. Rev. Lett. **86**, 5341 (2001).
[5] S. N. Taraskin, D. A. Drabold, and S. R. Elliott, Phys. Rev. Lett **88**, 196405 (2002).
[6] S. Goedecker, Phys. Rev. B **58**, 3501 (1998).
[7] X. Zhang and D. A. Drabold, Phys. Rev. B **63**, 233109 (2001).

[8] R. Delves and G. Joyce, J. Phys. A: Math. Gen. **34**, L59 (2001).
[9] H. Ehrenreich and L. Schwarts, Solid State Phys. **31**, 149 (1976).
[10] I. Gradshteyn and I. Ryzhik, *Table of Integrals, Series and Products* (Academic Press, San Diego, 2000), 6th ed.